

A new method to measure partial molar volumes of binary gas mixtures

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Abstract

An extraordinary new method has been developed to measure partial molar volumes directly and without differentiation of the experimental results. The potential of this method to measure volumes of mixing was identified whilst modifying a perturbation viscometer to work with non-ideal gas mixtures.

The method employs an apparatus, which is a descendent of the capillary viscometer. In it the flow and composition of a gas mixture flowing through a capillary are perturbed by the addition of a small flow of gas, normally one of the pure components of the gas mixture. Pressure changes are seen at the capillary due to the change in volumetric flowrate and the change in viscosity. For ideal gas mixtures the flowrate change when the perturbation is added is simply the volumetric flow of the added gas. For non ideal gas mixtures when the perturbation is added the volumetric flowrate change is not exactly the same as the added volumetric flowrate because the molar volume of the mixture changes. If a 'slug' of gas with the same composition as the mainflow is pushed into the mainflow in front of the pure component perturbation flow, the true volumetric increase in flow is observed. Once the 'slug' of gas has been added an additional change is observed due to the change in molar volume of the main flow, which results from the pure component perturbation flow mixing into the main flow.

This method uses the ratio of the pressure change at the capillary viscometer due to molar volume change of mixing to the pressure change due to the increase in flow to calculate the partial molar volume of the pure component used to perturb the main flow. If both pure components are used separately to perturb the same mainflow in turn then both partial molar volumes can be determined directly and used to deduce the molar volume of the mixture. The method requires that the molar volumes are known for both of the pure components of the mixture.

Results have been obtained for partial molar volumes of helium–pentafluoroethane mixtures at 23°C. The results obtained show that the method is both highly sensitive and precise.

Partial molar volumes are conventionally determined from density measurements for gas mixtures. Typically the excess volume change on mixing is calculated from the density data, then fitted with a polynomial normally of the Redlich Kister type. The necessary derivatives are then found analytically. We report here a new method, which is more accurate because it measures the partial molar volumes directly. The method has been developed as a by-product of modifications made to a perturbation viscometer to measure viscosities of non-ideal gas mixtures. Extra measurements were made with the viscometer which were used to correct the viscosity measurements for non-ideal behaviour. These extra measurements then posed two questions: What are we measuring? And can we use it? What follows is the theory that answers some of these questions. In other words we did not think of this method but discovered it.

The apparatus used is a development of the Russell et al (2003) a viscometer designed to make measurements on mixtures of gases containing at least one non-ideal component. The apparatus has been designed to run at temperatures down to -30°C to accentuate non-ideal behaviour of the gas mixture.

A simplified schematic drawing of the new apparatus is shown in Figure 1 and a typical pressure record for an experiment is given as Figure 2. The experiment is summarised here to identify the measurements of interest. A typical experimental run starts with a main molar flow M of gas of composition X_i^0 passing through valve 2, the ambient temperature delay line, next a cold delay line and finally the measuring capillary. Valve 1 is set to deliver a perturbation flow of gas composition X_i^0 to valve 2. Valve 2 is set to deliver the perturbation flow into a purge stream at the same conditions as the main experimental flow. This arrangement fills the transfer line between the two valves with gas of composition X_i^0 .

Valves 1 and 2 are switched simultaneously. The volume of gas in the transfer line composition X_i^0 is pushed in the main flow causing an increase in flow through the apparatus without a change in composition and the pressure rise $P_1 - P_0$ is observed at the measuring capillary. The gas in the transfer line is pushed as a 'slug' of gas (about 1 minutes duration) in to the main flow. The composition of the perturbation flow being added to the main flow then changes to X_i^T . The volume of gas in the system changes as the main flow and perturbation flow mix causing the next pressure change $P_2 - P_1$. The subsequent pressure changes relate to thermal expansion of the gas and viscosity changes described in full by Russell et al (2003)c.

The pressure changes observed represent the change in pressure at the upstream end of the measuring capillary. The pressure drop across the capillary can be described by the Poiseuille equation for laminar flow

$$\Delta P = \frac{128}{\pi} \frac{l}{d^4} \mu Q \quad (1)$$

For these pressure changes the viscosity is constant the pressures are therefore directly proportional to flows; thus the viscometer acts as a very sensitive flowmeter. The pressure changes can be arranged as a dimensionless flow ratio R

$$R = \frac{P_2 - P_1}{P_1 - P_0} = \frac{v_2 - v_1}{v_1 - v_0} \quad (2)$$

Where $v_1 - v_0$ is the change in flow caused by adding the perturbation

$$v_1 - v_0 = M\bar{V}^0 + m\bar{V}^T - M\bar{V}^0 \quad (3)$$

Where M and m are molar flows and the $\bar{}$ indicates molar volume
 $v_2 - v_1$ is the change in flow when the perturbation is mixed

$$v_2 - v_1 = (M + m)(\bar{V}^0 + \Delta\bar{V}) - M\bar{V}^0 - m\bar{V}^T \quad (4)$$

At this point we must consider the mode of operation of the viscometer. The size of perturbation will determine what is actually being measured

Theory for calculations from experiments using small perturbation flowrates

We are aiming to measure the gradient of the molar volume-composition curve. For small perturbation flows added to different compositions of main gas flow see Figure 3 which presents an experimental result for addition of a perturbation of component A to a main flow composition X_i^0 on a graph of molar volume as a

function of composition. Our goal function is therefore $\frac{\Delta\bar{V}}{\Delta X_i}$ which tends to the limit

case $\frac{d\bar{V}}{dX_i}$ if the perturbation flows are small enough. Rearranging expression 4 to give

an equation $\Delta\bar{V}$ for begins the analysis and

$$\Delta\bar{V} = \frac{v_2 - v_1}{M + m} - \frac{m(\bar{V}^0 - \bar{V}^T)}{M + m} \quad (5)$$

The composition change is found by performing a mass balance across the perturbation valve

$$M(X_i^0) + m(X_i^T) = (M + m)(X_i^0 + \Delta X_i) \quad (6)$$

Which rearranges to give

$$\Delta X_i = \frac{m}{(M + m)}(X_i^T - X_i^0) \quad (7)$$

5 and 7 are combined to give

$$\frac{\Delta\bar{V}}{\Delta X_i} = \frac{1}{(X_i^T - X_i^0)} \left(\frac{v_2 - v_1}{m} - (\bar{V}^0 - \bar{V}^T) \right) \quad (8)$$

and m is eliminated using equation 3

$$\frac{\Delta \bar{V}}{\Delta X_i} = \frac{1}{(X_i^T + X_i^0)} \left(\left(\frac{v_2 - v_1}{v_1 - v_0} \right) \bar{V}^T - (\bar{V}^0 - \bar{V}^T) \right) \quad (9)$$

which simplifies to

$$\frac{\Delta \bar{V}}{\Delta X_i} = \frac{1}{(X_i^T + X_i^0)} \left((1 + R) \bar{V}^T - \bar{V}^0 \right) \quad (10)$$

let us examine Figure 3. We can use this figure to define a relationship for the gradient in terms of the partial molar volume \tilde{V}_A .

$$\frac{\Delta \bar{V}}{\Delta X_i} = \frac{\tilde{V}_A - \bar{V}^0}{(X_i^T + X_i^0)} \quad (11)$$

combination of equations 10 and 11 gives

$$\tilde{V}_A = (1 + R_A) \bar{V}^T \quad (12)$$

Similarly for a perturbation of component B

$$\tilde{V}_B = (1 + R_B) \bar{V}^T \quad (13)$$

and the total molar volume of the mixture is obtained by

$$\bar{V}_{mix} = X_A \tilde{V}_A + X_B \tilde{V}_B \quad (14)$$

Theory for calculations from experiments using large perturbation flowrates.

The viscometer can be operated in a different mode which uses large perturbation flows of one component to perturb main flows of the second. E.g. for main flow of component A, perturbation flows of gas B, increased from 1% to 100 % of the main gas flowrate, are added. By increasing the perturbation flow molar volumes are measured for different compositions (see Figure 4). For example if a perturbation flow equal to the main flow of gas is used the molar volume change to the centre of the composition range is measured. The molar volumes are calculated by adding the volume ratio to the molar volume of the main flow gas

$$\bar{V}_{mix} = \bar{V}_A + R_A \quad (15)$$

This method is crude and more susceptible to errors from the following causes

- 1) End effects on the measuring capillary
- 2) Entrance length effects on the measuring capillary
- 3) Compression effects within the measuring capillary
- 4) Non parabolic flow in the helical coils of the capillary

These effects can be compensated for but each correction will introduce some error. To generate the partial molar volumes from these data the traditional approach outlined earlier is required. The small perturbation method is therefore the preferred one but the large perturbation method is useful as a check on the data and for trouble shooting the experiments.

Experiment apparatus

The experimental apparatus is based upon the viscometer described by Russell et al. (2003). A detailed schematic flowsheet of the apparatus is shown in Figure 4. The design of the apparatus is summarised here with particular attention paid to the modifications made to facilitate these measurements.

The apparatus adopts a two-sided arrangement similar to that employed in gas chromatography. The pressure changes are measured differentially between the measurement gas flow and a reference gas flow. Any effects due to transient variations in flow and pressure are unseen by the pressure transducer because they affect both sides equally.

A flow setting block has been designed to provide four equal very stable matched flow streams, one measurement flow, one reference flow and two purge flows. The block has sufficient thermal mass and conducts heat well enough to maintain all components of the block at the same temperature. A single stream of gas mixture at fixed pressure is supplied to the block, which splits the gas flow internally into four equal gas flows by using a *Porter* high-resolution non-rising-stem needle valve followed by a *Porter* laminar flow element in each path. The laminar flow elements provide almost matched flowrates. The fine-control valves are used as trimmers. The pressure drop across the block is about 0.2 bar and this delivers a flow of about 4 ml/min through each side of the apparatus.

When adding or removing the perturbation flow, sharp deviations in pressure occur unless the pressures on both sides of addition valve are exactly equal. This apparatus uses two perturbation flows one at composition X_i^T and a second at X_i^0 . In order to try to keep the pressure in each perturbation stream exactly the same as the main flow, each perturbation flow, flows into its own purge stream when it is not added to the mainflow. The geometry of the pipework for each purge flow must be similar to that for the main flow and connected to the same outlet back-pressure regulator to give matched pressure drops.

Downstream on the measurement side of the apparatus is the perturbation switching system. The design of this system is important to the overall operation of the apparatus, particularly when precision measurements are being made. It is the only difference between the measurement side and reference side of the apparatus and therefore has the possibility of introducing systematic errors.

The switching assembly, is comprised of two electrically actuated valves 4PSV-5 and 3PSV-3 connected together by 0.5 metres of 0.020 inch bore Silco steel tube. Both valves are electrically actuated to give a smooth repeatable switching action not possible with manually actuated valves. The connecting tube is sized to hold a 'Slug' of gas of composition X_i^0 which can be pushed into the main flow in front of the perturbation flow, composition X_i^T . This separates out the pressure change for the change in flowrate from that due to volume change on mixing by delaying the onset of mixing of the two flows by 1 minute.

Valve 4PSV-5 is a standard electrically actuated 1/16 inch Valco, 4 port, 2 position valve. It is used to select either a perturbation flow of gas of composition

X_i^0 or the normal perturbation flow composition X_i^T . The perturbation flow of gas of composition X_i^0 is used to purge out the silcosteel transfer line between the valves at the start of an experiment. It is supplied to valve 4PSV-5 from massflow controller MFC-5 that sets and controls this flowrate. MFC-5 has been modified with a bypass so that the composition can be changed quickly even though the metered flow is very low. The perturbation flow of gas of composition X_i^T is supplied to selection valve 4PSV-5 from the existing perturbation supply system.

Valve 3PSV-3 is a 1/8 inch Valco, 3 port, 2 position valve, used to add the perturbation flow to the measurement flow. This is a special low-pressure drop valve, its bore being 1/16 inch, the same as the standard tube used throughout the rest of the apparatus. The valve body has been modified to achieve flow-through operation by machining two additional ports into the valve at 90° to the two gas supply ports. These have been joined to the bases of the original ports by 1/16 inch diameter drillings. The new ports have been tapped to take *Swagelok* 1/8 to 1/16 inch stainless steel reducing unions, which have been, bored through to a diameter of 1/16 inch and sealed with rubber “O” rings. The bore of the valve assembly carrying the main flow is never less than 1/16 inch and is matched by an extra length of 1/16 inch bore tubing in the reference side of the apparatus. Both streams thus have very similar dynamic behaviour.

Two delay lines, which separate the flow, and viscosity pressure affects connect the two main flows to opposite sides of the pressure transducer. A *Furness* differential, pressure transducer (DPT) of 10 mm H₂O range is used to measure the pressure changes. Downstream of the pressure transducer an additional pair of delay lines followed by the flow sensing capillaries are mounted inside cold aluminium block. To ensure thermal stability, the capillaries are wound onto a nickel core. The aluminium block is cooled directly by a Peltier chiller and is insulated with 50 mm of polyurethane foam to give temperature control to better than 0.1 °C. The temperature difference between the capillaries is very much smaller than this. After the capillaries the flow streams are joined back together and vent to atmosphere via a dome-loaded backpressure regulator.

Experimental Results

The experimental results reported here were derived from the experimental pressure records measured for the viscosity experiments reported by Russell et al (2003)c. All measurements for partial molar volumes were made at 23 °C the ambient temperature of the laboratory. Note the valve where the measurements are made is not temperature controlled. Both gases were supplied by BOC. The helium was supplied as 99.99% purity and the suva-125 as 99.0% purity. Two sets of data are reported where small perturbation flows of each of the two pure gases were used to perturb main flow compositions at nominal 0.1 mole fraction intervals across the composition range. The main flow gas mixtures were prepared using a gas blender of our own design. A second set of data using large perturbation flows of each pure gas to perturb main flow of the second component. These results were used to check that the data were correct for this mixture because no other sources of experimental data for this mixture could be found.

Figure 5 presents the calculated partial molar volumes at 23°C obtained from both sets of small perturbation experiments. The sets agree remarkable well given that there is no temperature control on the apparatus. Simple polynomials that generate the curves seen in Figure 5 have been fitted to the data. These functions have been used to

generate the molar volume composition function presented in Figure 6. Two sets of data points produced using large perturbations are also plotted. These show remarkable agreement with the small perturbation data; indeed any deviations are not systematic and within the random scatter of the results. To check that the data are consistent with other sources values have been predicted using the Redlich Kwong and Redlich Kwong Soave equation of state. The critical constants for these equations were obtained from the NIST Chemistry WebBook. Our results lie between the boundaries of these two predictions, which suggest they are both correct, and of a much higher precision.

Conclusions

A new and we believe unique method to measure the partial molar volumes for gas mixtures has been presented. The method has been shown to produce high quality results that are both internally consistent and better than can be predicted using simple three parameter equations of state. The method can be easily modified to run at elevated temperatures and pressures and should become the way of making these measurements.

Notation

G	logarithmic viscosity gradient
m	molar flow rate of perturbation gas
M	molar flow rate of main-flow gas
P_0	pressure at gauge before perturbation flow added
P_1	pressure at gauge after perturbation flow added
P_2	pressure at gauge after viscosity change has occurred
P_3	pressure at gauge after perturbation flow removed
P_4	pressure at gauge after viscosity change has occurred
Q	volumetric flowrate of main flow
q	volumetric flowrate of perturbation flow
R	ratio of viscosity pressure change to flow pressure change
T	temperature
\bar{V}	molar volume
X	mole fraction
<i>Greek symbols</i>	
μ	viscosity
Δ	a small but finite difference
<i>subscripts</i>	
He	helium
Suva-125	Suva-125
i	species i
add	adding perturbation
rem	removing perturbation
calc	value calculated from polynomial fitted through all measured gradients
<i>superscripts</i>	
0	main flow gas
T	perturbation gas

References

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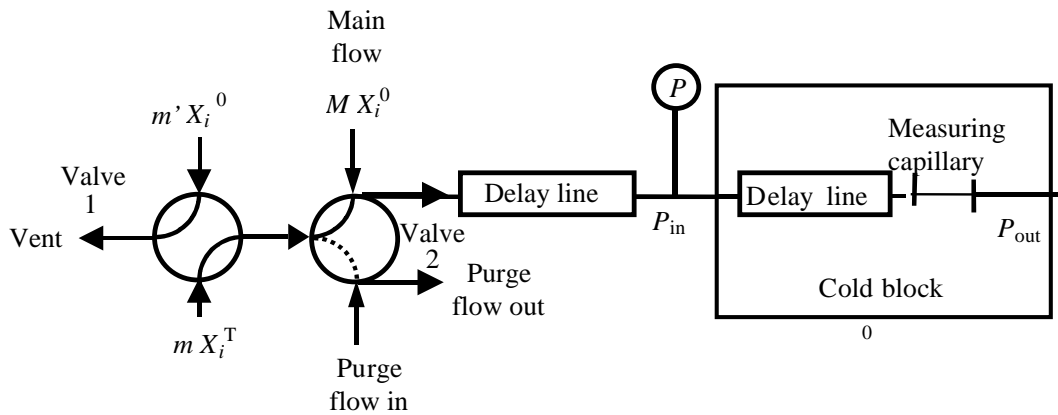


Figure 1 Diagram of the new non-ideal gas apparatus. In normal operation a (main) flow of gas, M of known composition X_i^0 , flows through valve 2 then an ambient temperature delay line (low resistance empty tube), a cold delay line and finally the measuring capillary tube. In an experiment a small perturbation flow is added to the main flow and the responses are observed at the pressure gauge. Further measurements are made when the perturbation flow is removed.

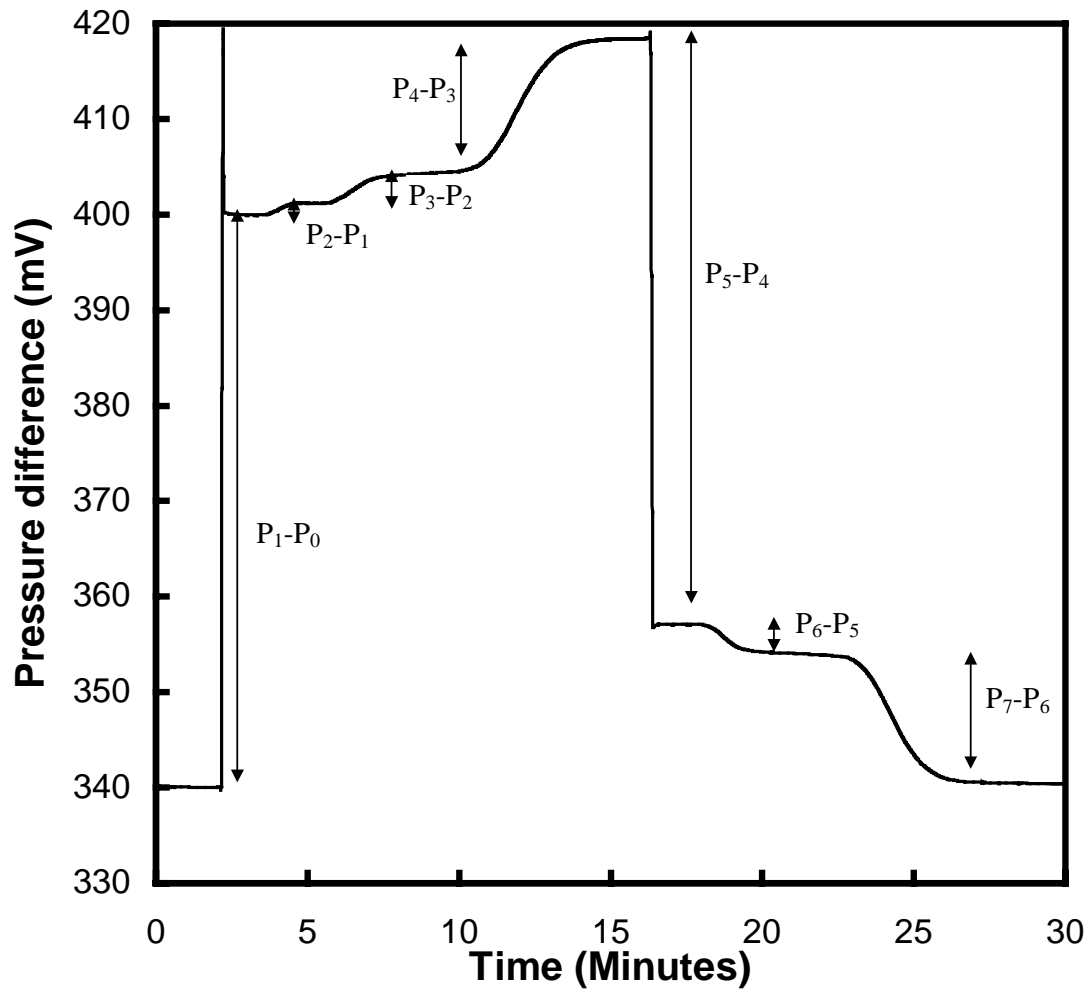


Figure 2 The actual pressure record for an experimental run at -23°C where a perturbation flow of helium was added to, then removed from a HFC-125 main gas flow. The pressure changes are: Step1 P_0 to P_1 due to increase in flow when perturbation is added; Step2 P_1 to P_2 Volume change on mixing of the two gas flows; Step3 P_2 to P_3 Change in thermal expansivity of gas in cold block; Step4 P_3 to P_4 increase in viscosity due to increase in helium mole fraction; Step5 P_4 to P_5 decrease in flow when perturbation is removed; Step6 P_5 to P_6 Change in thermal expansivity of gas in cold block; Step7 P_6 to P_7 increase in viscosity due to decrease in helium mole fraction.

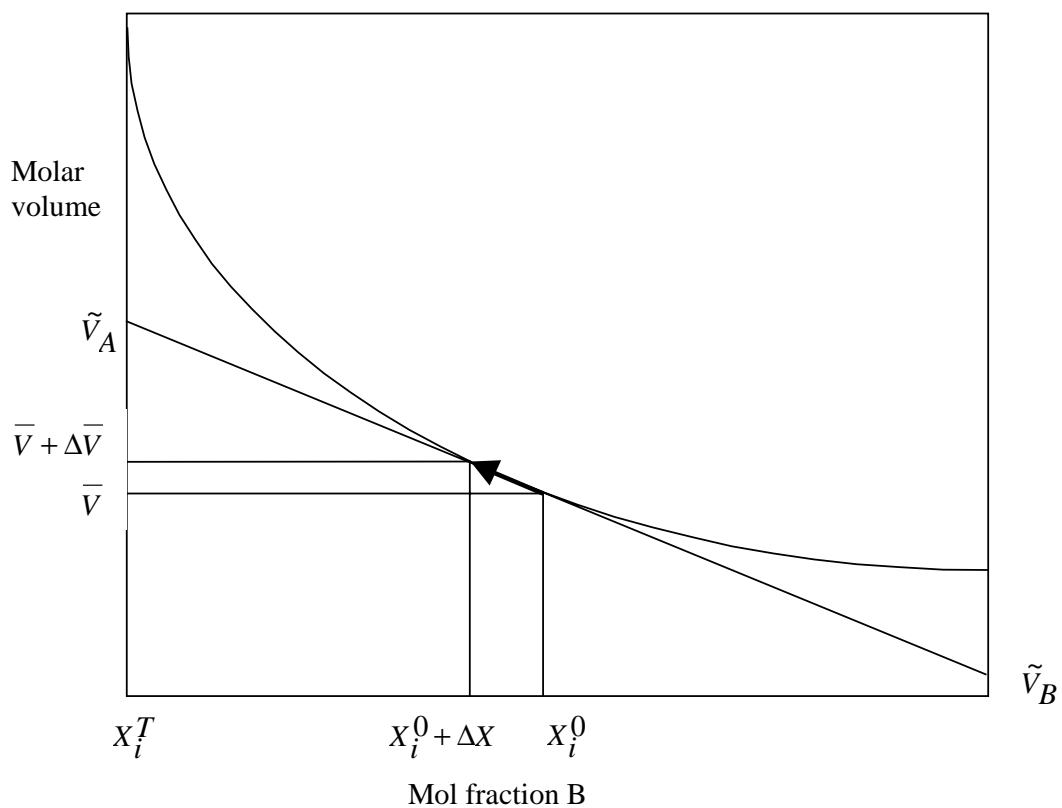


Figure 3 graph of molar volume-composition function. Black arrow represents measurement made by small perturbation experiment tangent to the curve is drawn at starting composition for experiment. Extreme ends of the tangent indicate the partial molar volumes for this mixture.

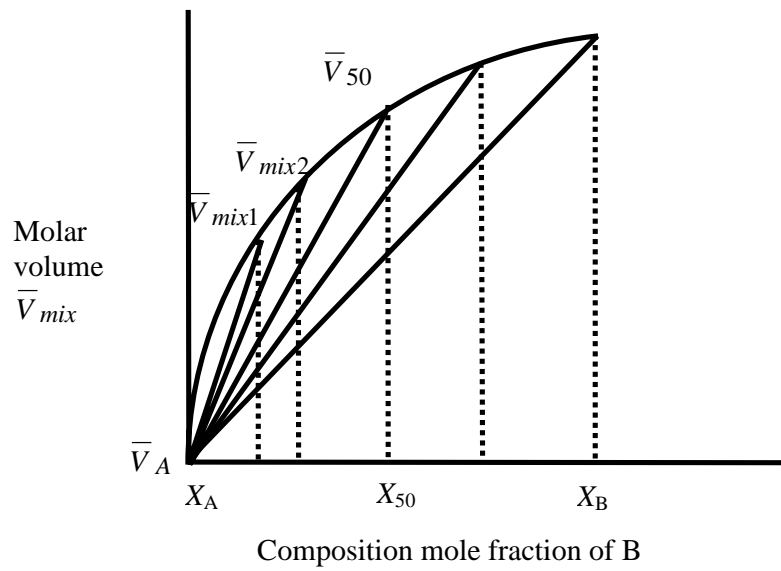


Figure 4 Diagram showing how by increasing the flowrate of the perturbation used changes the composition at which the molar volume is measured.

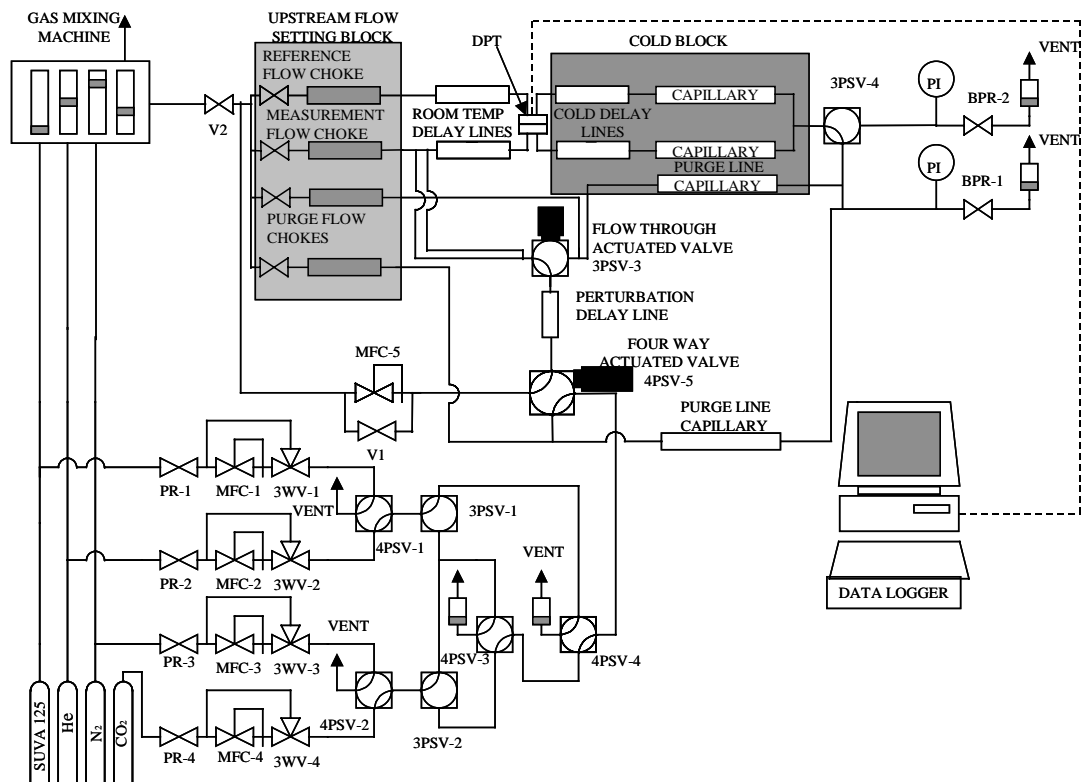


Figure 4 Schematic flow diagram of new experimental apparatus. BPR-1, BPR-2 and BPR-3, Modified downloaded back pressure regulators based on *Porter Instruments* 9000; DPT , *Furness Controls* FCO 40 differential pressure transducer; MFC-1,MFC-2, MFC-3 and MFC-4, *Porter Instruments* VCD 1000 flow controllers PR1,PR2,PR3 and PR4, modified *Porter Instruments* 8286 pressure regulators; 3PSV-1, 3PSV-2, 3PSV-3 and 3PSV-4, *Valco* UWE three port switching valves; 4PSV-1, 4PSV-2, 4PSV-3, 4PSV-4 and 4PSV-5, *Valco* UWE three port switching valves; 3WV-1, 3WV-2, 3WV-3 and 3WV-4, *SSI* 02-0182- , Swagelok series 40 ball valves: V1 and V2

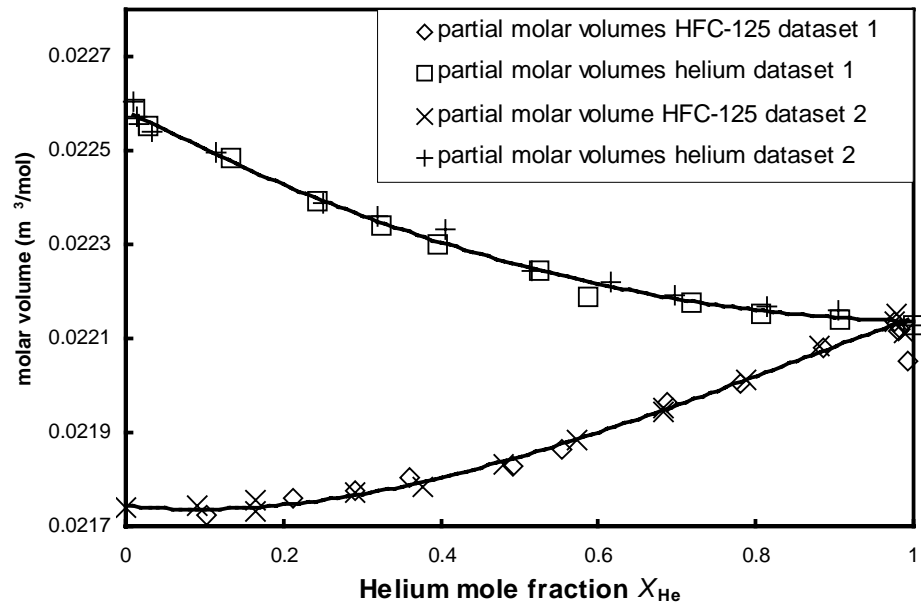


Figure 5 The calculated partial molar volumes at 23°C and 1.11 bar(absolute) obtained from both sets of small perturbation experiments.

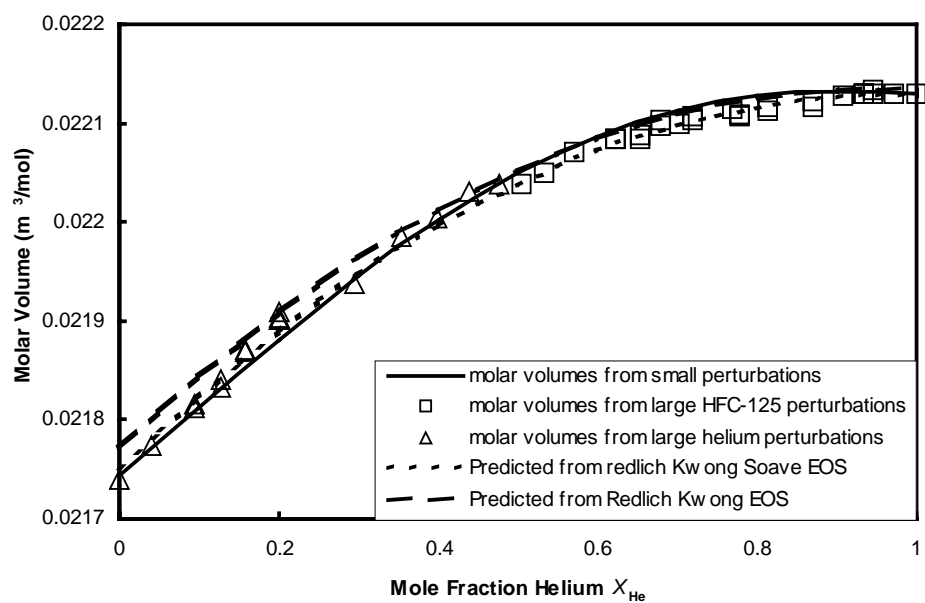


Figure 6 Plot showing the molar volume of the gas mixture helium–sulfur dioxide as a function of helium mole fraction at 23°C and 1.11 bar(absolute).